CONCENTRATION OF BIOPETROL FROM PALMITIC ACID

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DECLARATION

I declare that this thesis entitled *"Concentration of Biopetrol from Palmitic Acid"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ……

Name : Noor Zariyati Binti Mohammad

Date : APRIL 2008

DEDICATION

To my beloved parents and siblings,

ACKNOWLEDGEMENT

First of all, I like to express my gratitude to Ilahi because giving me a good health condition during the period of finishing this project. Opportunities doing this project have taught me many new things. There is fun and sad time, but I relieved that there is always people around me when I am in need and I would like to thank them from the bottom of my heart.

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Thank you.

ABSTRACT

Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. The objective of this study is to find the concentration of biopetrol (isooctane) from palmitic acid. Thermal cracking process is used to produce isooctane from palmitic acid. Heat is supplied using hot plate at palmitic acid's melting point within a range of 63^{o}C – 64^{o}C, to melt the solid palmitic acid. After it turns to liquid, the heating is continuous at isooctane's boiling point of 98^{o}C by using heating mantel 250ml to form new arrangements of carbon compounds including isooctane. The heating is continuous and the sample was collected at temperature 200^{o}C, 300^{o}C, 330^{o}C and 350^{o}C. The desired isooctane obtained is around 0.0455% - 0.0743% in the distilled palmitic acid. After the back calculation, the highest concentration of the desired isooctane is 2.92% at temperature 350^{o}C palmitic acid.

ABSTRAK

Biopetrol didefinasikan sebagai bahan bakar yang mempunyai formula molekul yang sama dengan petrol biasa. Tujuan projek ini dijalankan adalah untuk mengenalpasti kepekatan biopetrol (isooktana) di dalam asid palmitik. Kaedah penghuraian haba digunakan untuk mendapatkan isooktana daripada asid palmitik. Pepejal asid palmitik dipanaskan pada suhu di antara 63^{o}C – 64^{o}C, iaitu pada takat lebur asid palmitik. Kemudian proses pemanasan diteruskan sehingga mencapai takat didih isooktana, iaitu 98^{o}C untuk membentuk susunan molekul karbon yang baru. Kemudian pemanasan diteruskan sehingga mencapai suhu 350^{o}C. Sampel diambil pada suhu 98^{o}C, 200^{o}C, 300^{o}C, 330^{o}C dan 350^{o}C. Kepekatan isooktana yang diperolehi di dalam didihan asid palmitik adalah dalam lingkungan 0.0455% - 0.0743%. Kepekatan tertinggi adalah pada suhu 350^{o}C didihan asid palmitik iaitu sebanyak 0.0743%. Selepas mengira semula kepekatan isooktana tanpa pencairan heksana, kepekatan tertinggi adalah pada suhu 350^{o}C iaitu sebanyak 2.92% dan hasil keputusan ini dapat ditingkatkan dengan mengunakan kaedah yang lain seperti penghuraian dengan menggunakan agen pemangkin.

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P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
n	-	Number of moles
L	-	Liter

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CHAPTER 1

INTRODUCTION

1.0 Introduction

Since the price of petrol increases as well as decreasing of petrol or petroleum supply, more researches are done to find the alternative fuel as substitution of petroleum-based fuel, including biodiesel and biopetrol. Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. Biodiesel, which consists methyl esters has been already developed from vegetable oils and commercialized. However, biodiesel is only suitable for diesel engine.

Producing petrol from the waste of palm oil (palmitic acid) will give an alternative choice to the users, especially for petrol-engine vehicles' owners. In addition, this biopetrol, which is graded 100 for its octane number, burns very smoothly so biopetrol can reduce emissions of some pollutants (Omar, 2005).

This study is to find the concentration of isooctane as the main component of petrol from palmitic acid (palm oil waste). The method that used is cracking method that is applied in petroleum industries.

1.1 Problem Statement

Petroleum price is increasing dramatically year by year and it will burden people especially to the lower working class. This is because of decreasing fuel supply and the sources are unevenly spread. Most petroleum reserves are in the Middle East or West Asia, causing economic and political instabilities.

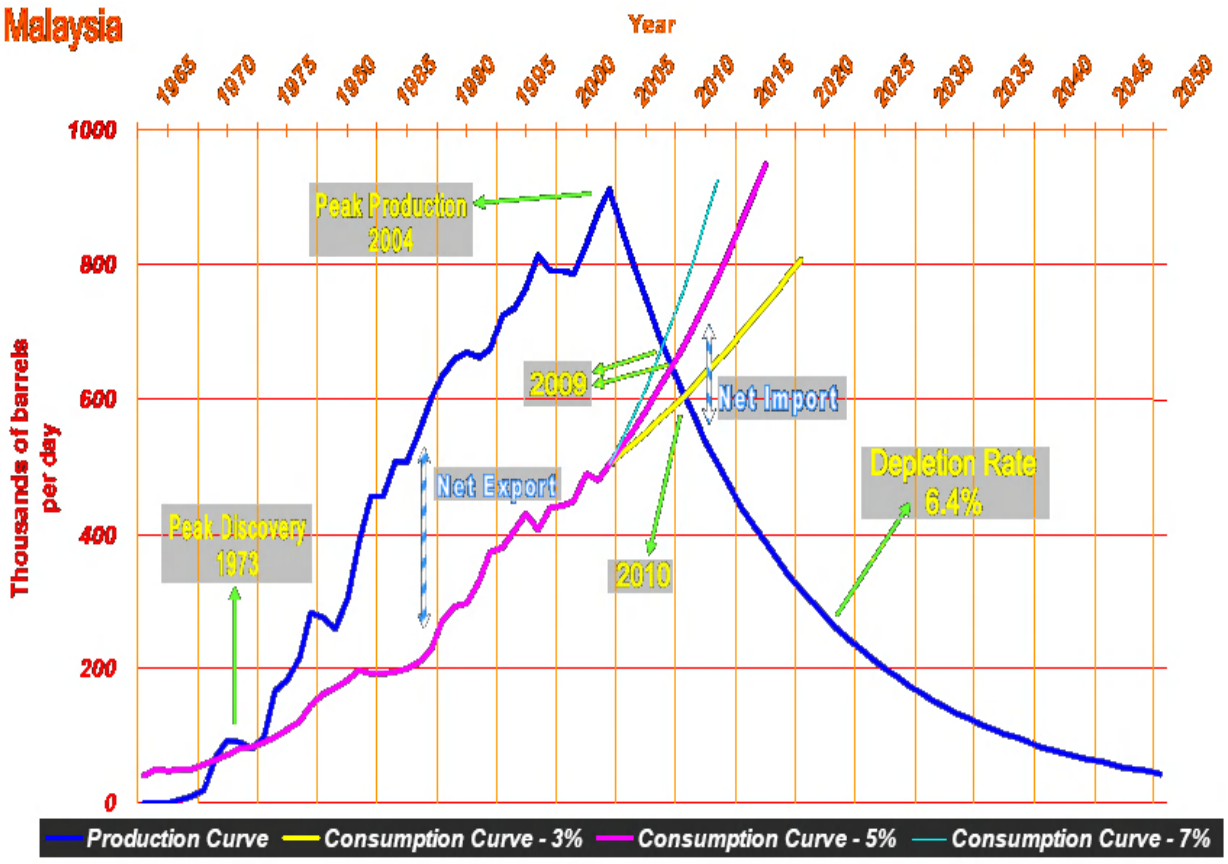

Figure 1.1 : Malaysia's Looming Energy Crisis (M. Noor, 2008)

Malaysia is the one of the major oil exporters in the world. Malaysia also has the crisis of the declining of these mineral sources. Malaysia's oil production is decreases in 2004 and would then decline by 6.4 percent annually. Figure 1.1 shows the declining Malaysia oil's production by 2004. Forecast, by 2009 to 2010 Malaysia will become a net importer because out of mineral sources (petroleum) and the demand of oil increasing.

Producing petrol from the waste of palm oil (palmitic acid) will give an alternative choice to the users, especially for petrol-engine vehicles' owners. In addition, this biopetrol, which is graded 100 for its octane number, burns very smoothly so biopetrol can reduce emissions of some pollutants (Omar, 2005).

Palmitic acid is the dominative component in palm oil waste. Its disposal into water supply sources causes serious water pollution. Besides that the loss of palmitic acid as a useful industrial component also occurs so that it is not utilized much and always eliminated to improve and upgrade the quality of crude palm oil. Thus, it is disposed as palm oil waste and then pollutes water resources by its spillage.

The challenge of this research is this research will be outstanding at a time when palm-oil prices are going down, production is increase and the energy prices are ruling high.

In this research, the concentration of isooctane that is produced from palmitic acid and also the conversion of fatty acids form desired isooctane in biopetrol will be the objectives.

1.2 Objectives

- To analyze isooctane obtained from palmitic acid
- To find the concentration of biopetrol obtained from palmitic acid

1.3 Scopes

To achieve the objective, scopes have been identified in this research. The scopes of this research are listed as below:-

- To describe the molecular arrangement in cracking process.
- To understand the thermal cracking and distillation process.
- To identify the composition of isooctane using Gas Chromatography method with Gas Chromatographer.
- To determine the amount of isooctane in sample obtained using Gas Chromatography method as well.

CHAPTER 2

LITERATURE REVIEW

2.0 Definition of fuel

Fuel (from Old French feuaile, from feu fire, ultimately from Latin focus fireplace, hearth) is a substance that may be burned in air (or any other oxidant-containing substance), which so quickly reacts with oxygen that heat and light is emitted in the form of a sustained flame. Oxygen in the air is the basic oxidant for and is readily available from Earth's atmosphere; that is why it is the main oxidizer. Fuels are used as convenient energy stores because of their high specific energy release when burnt with omnipresent ambient air.

2.1 Uses of fuel

Fuel is used as convenient energy stores because of their high specific energy when burnt with omnipresent ambient air. Primary (natural) fuels may be difficult to find in Nature, and secondary (artificial) fuels may be difficult to be manufactured, but, once at hand, fuels are very easy to store, transport and use, with the only nuisance of safety (uncontrolled combustion) and pollution such as toxic emissions during storage and when burnt.

Energy is a basic need to humans and is used for heat generation, for work generation, or for chemical transformations. A common problem to all human needs (except air, in most cases) is that energy is not available at the location and time we desire, and sources must be found (for energy, water, food, minerals) and transportation to a better place must be arranged, as well as storage and end-use details. Storage is sometimes the most cumbersome stage, for example for food (all food is perishable, particularly meat, fish, vegetables and fruits) and for electrical energy.

2.2 Fuel types by period of natural renovation

2.2.1 Fossil fuels

Fossil fuels (coal, crude-oil and natural gas) were formed slowly (during millions of years, mainly at certain remote epochs, not uniformly; for example American oil was formed some 90 million years ago, whereas the rest dates from 150 million years) by high-pressure-decomposition of trapped vegetable and animal matters during extreme global warming. Fossil fuels are found trapped in Earth's crust, up to 10 km depth, although large pressure might stabilise them also at higher depths and temperatures (at 300 km it might be 10 GPa and 1000 ºC). They are then non-renewable energy supply at humankind periods, and will eventually be commercially depleted. Table 2.1 below shows the estimated reserves and availability of fossil fuels.

Table 2.1 : Estimated reserves and availability of fossil fuels.

	Commercial reserve-2000	Reserve/Consumption-2000
Coal	$1000 \cdot 10^{12}$ kg	250 yr
Crude oil	$100 \cdot 10^{12}$ kg	40 yr
Natural gas	$150 \cdot 10^{12}$ kg.	70 yr

2.2.2 Petroleum fuel

More than 50% of world's primary energy comes nowadays from petroleum that is all vehicle fuels, and small and medium stationary applications fuels are petroleum derivatives, obtained by fractional distillation and reforming. Main commercial fuels and their physical data are presented in Table 2.2

Table 2.2 : Main commercial fuels derivatives from crude-oil, and their main averaged properties.

	Boiling range T_b [K]	Boiling range T_b [ºC]	Carbon chain range	Density (liquid at 15 ºC) ρ [kg/m^3]	Viscosity at 40 ºC $\nu \cdot 10^6$ [m^2/s]	Flash point T_{flash} [ºC]	Main use
Liquefied petroleum gases (LPG)	<300	<30	1-4	580	0.5	–100	domestic heating, cars
Gasoline	300-500	30-200	4-12	730-760	0.5	–30	cars
Kerosene	450-650	150-350	10-14	780-850	3	40	aircrafts
Diesel	500-600	200-300	10-20	820-880	3	40	cars, lorries, boats
Fuel oil distillate	600-800	300-500	15-30	840-930	10	60	industry, ships

2.2.3 Renewable fuel

Renewable resources include energy from sun, wind, flowing water, the earth's internal heat, and biomass. For example,

- Passive solar heating captures sunlight directly within a structure and converts it into low temperature heat for heating.
- Hydroelectric power supplies 20% of the world's power and 6 % of the total commercial energy.

Wind and solar power represent an ultimate in environmental sustainability. But the problem is the sun does not always shine and the wind may not blow when needed. Thus, the alternative renewable and environmental friendly sources of energy are biomass.

Biomass is organic material from living organisms, such as plant matter including trees, grasses, and agricultural crops that can be burned or converted to liquid or gaseous fuels for energy (Lim, 2006).

Biomass is formed in a year or a few years basis. Synthetic fuels may come from fossil or from renewable sources such as:

- Gas: biogas from anaerobic fermentation or flue gas from pyrolysis of biomass.
- Liquid: alcohols, ethers, liquid paraffins (biopetrol), esters (biodiesel).
- Solid: wood, charcoal, fuel pellets (from wood or vegetable residues), agricultural residues, cattle manure, urban waste.

2.3 Biological fuel

The terms of biofuels, biomass fuels and renewable fuels, may be used indistinctly if they refer to natural or artificial fuels obtained from renewable sources, although the other times distinctions are introduced and then biofuels may refer to biomass derivatives directly substituting fossil fuels for the same combustor, biomass may be restricted to unprocessed biomass (forest waste, crops and agriculture waste, animal waste, domestic waste), and renewable may include fuels like hydrogen obtained by electrolysis and not from biomass.

A 1999 biofuel life cycle study concluded that biofuel reduces net CO_2 emissions by 78% compared to petroleum fuel from biofuel's closed carbon cycle. The CO_2 released into the atmosphere from the combusted biofuel is recycled and reused by growing plants, which are later processed into fuel (Lee, 2006).

Scientific research confirms that biofuel has a less harmful effect on human health than petroleum fuel. Biofuel emissions have decreased levels of polycyclic aromatic hydrocarbons (PAHs) and nitrited PAH compounds (nPAH), which have been identified as carcinogenic (cancer-causing agent) compounds. The test results indicate that PAH compounds were reduced by 50 - 85%. Biofuel is nontoxic and biodegradable. Otherwise, the flashpoint (the lowest temperature at which it can form an ignitable mix with air) is 300 ^{o}F while petroleum fuel's flashpoint of 125 ^{o}F (Lee, 2006).

But the complete utilization movement to biofuels is not based on their short-term advantage over fossil fuels but on the long-term need to have fuels of any kind. And for the time being, living matter and their residues are a handy alternative to recover the non-renewable fossil fuels.

2.3.1 Classes of Biofuels

2.3.1.1 Solid Biofuels

There are many forms of solid biomass that are combustible as a fuel such as:

- Wood
- Straw and other dried plants
- Animal waste such as poultry droppings or cattle dung
- Crops such as maize, rice, soybean, peanut and cotton (usually just the husks or shells) & sugarcane- or agave-derived bagasse.

2.3.1.2 Liquid Biofuels

There are also a number of liquid forms of biomass that can be used as a fuel:

- Bioalcohols
  - Ethanol – usually produced from sugarcane, also from corn
  - Methanol, which is currently produced from natural gas, can also be produced from biomass. The methanol economy is an interesting alternative to the hydrogen economy
  - Butanol, formed by A.B.E. fermentation (Acetone, Butanol Ethanol) and experimental modifications of the ABE process show potentially high net energy gains. Butanol can be burned "straight" in existing gasoline engines (without modification to the engine or car), produces more energy and is less corrosive and less water soluble than ethanol, and can be distributed via existing infrastructures.

- Biologically produced oils (bio-oils) can be used in diesel engines
  - Straight vegetable oil (SVO)
  - Waste vegetable oil (WVO)
  - Biodiesel obtained from transesterification of animal fats and vegetable oil, directly usable in petroleum diesel engines

- Oils produced from various wastes
  - Thermal depolymerization from waste materials can extract methane and oil similar to petroleum
  - Methane and oils are being extracted from landfill wells and leachate in test sites

2.3.1.3 Gaseous Biofuels

- Bio-methane produced by the natural decay of garbage or agricultural manure can be collected for use as fuel
  - It is also possible to estimate the number of animals needed for desirable size of biogas driven engine with Biogas Calculator
- Wood gas can be extracted from wood and used in petrol engines.
- Hydrogen can be produced in water electrolysis or, less ecologically, by cracking any hydrocarbon fuel in a reformer, some fermentation processes also produce hydrogen, such as A.B.E. fermentation
- Gasification, that produces carbon monoxide.

2.3.2 Biofuel From Palm Oil.

Palm oil is a superior biofuel sources compared to other vegetable oils. This is due to its availability, and the fact that is able to be produced on a positive energy balance, compared to other competing vegetable oils.

Palm oil is called as a very energy-efficient raw material. The energy output and input ratio is nine to one, compared to three to one for corn, soy, and rapeseed. Palm oil is a real energy factory, whereas these other crops have a very low output to input energy ratio.

2.3.2.1 Price of Palm Oil

DBS Vickers Research has raised its crude palm oil (CPO) price forecast for 2008 to RM 2,650 per tonne. This is higher than the previous RM 2,500 forecast and is said to be due to a potential supply shortage. DBS Vickers Research has raised its crude palm oil (CPO) price forecast for 2008 to RM 2,650 per tonne. This is higher than the previous RM 2,500 forecast and is said to be due to a potential supply shortage.

Ben Santoso, DBS Vickers' plantation analyst in Indonesia said that crude palm oil prices will remain buoyant through the first half of next year as much of the global oil seeds output has been adversely affected by the drought in many oilseeds producing countries.

Oil World, an independent agency offering analyses and forecasts of supply, demand and price for oil seeds industries indicated that production deficits will most likely put pressure on prices next year.

Malaysia, the world's leading palm oil producer had already estimated lower output this year although it expected export revenue to be a record RM 40 billion this year due to rising product prices.

Demand for CPO is expected to rise as rising crude oil prices and environmental concerns prompt consumers to make the switch to greener energy such as biodiesel.

2.3.2.2 Palm Oil Waste

Large quantities of palm waste called Empty Fruit Bunches (EFB) are available from plantations where palm oil is produced. In its raw state, EFB is both very fibrous and wet. EFB is a solid waste produce from oil palm milling process and has high moisture content. The treated empty bunches are mechanically crushed (de-watered and de-oiled) in the process. EFB is rich nutrients and contained reasonable amounts of trace elements. EFB have a value when returned to the field to be applied as mulch for the enrichment of soil. However, it was noted that over application of the effluent must be avoided as it may result anaerobic conditions in the soil by formation of an impervious coat of organic matter on the soil surface (Mansur, 2005). Thus, used of EFB to become biofuel can reduce the amount of waste, lower cost and can reduce the pollution.

2.4 Biofuel production methods

In Japan, bacteria has been bred which produces ethanol from paper or rice-straw without any pre-treatment. There are some methods to produce biofuel:

- Methane (actually a biogas mixture) by anaerobic digestion of biomass waste (manure, straw, sewage, municipal solid waste (MSW)).

- Oils (biodiesel) by reforming oleaginoseous plant seeds (e.g. colza, sunflower, soy). The marine microscopic algae Botryococcus Braunii has been shown to accumulate a quantity of hydrocarbons amounting to 75% of their dry weight.
- Methanol from wood-waste distillation.

For mobile applications, because of higher energy density and simpler infrastructure, liquid biofuels are preferred (ethanol and biodiesel), gaseous biofuels being restricted to stationary applications. As an aid in transition from fossil fuels to biofuels, mixtures of both fuels and biofuels are being progressively put on the market for old engines and combustors, and new engines and combustors are progressively developed to run on 'biofuel prototypes' derived from current fossil fuels.

2.4.1 Biodiesel

Biodiesel refers to any diesel-equivalent biofuel made from renewable biological materials such as vegetable oils or animal fats. While there are numerous interpretations being applied to the term biodiesel, the term biodiesel usually refers to an ester, or oxygenate, made from the oil and methanol (in other words, the name ''biodiesel'' can be applied to any transesterified vegetable oil that makes it suitable for use as a diesel fuel).

Technically, as mentioned earlier, biodiesel is vegetable oil methyl ester , or in general one could say that biodiesel consists what are called mono alkyl-esters. It is usually produced by a transesterification and esterification reaction of vegetable or waste oil respectively with a low molecular weight alcohol, such as ethanol and methanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin (soap). Once the glycerin is removed from the oil, the remaining molecules are, to a diesel engine, somewhat similar to those of petroleum diesel fuel. There are some notable differences though. While the petroleum and other fossil fuels contain sulfur, ring molecules & aromatics, the biodiesel molecules are very simple hydrocarbon

chains, containing no sulfur, ring molecules or aromatics. Biodiesel is thus essentially free of sulfur and aromatics. Biodiesel is made up of almost 10% oxygen, making it a naturally "oxygenated" fuel.

The concept of using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Diesel demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel.

Bio-diesel can be used in diesel engines either as a standalone or blended with petro diesel. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. For example, fuel containing 20 % biodiesel is labeled B20. Pure biodiesel is referred to as B100.

2.4.2 Biopetrol

Gasoline or petrol is a complex mixture of hydrocarbons which consists a mixture of C_4 to C_{10} alkanes. However isooctane ($C_{18}H_{18}$) as dominative component in petrol is assigned an octane number of 100. Isooctane or 2, 2, 4-trimethylpentane ($CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$) is burns smoothly with a little knock in petrol engine. It is the highest quality of petrol (Mansur, 2005).

The other alternative to produce petrol is by using biopetrol. Biopetrol is defined as fuel which has the same characteristics with the commercial petrol in terms of its molecular formula.

2.4.2.1 Biopetrol in The Future

Biopetrol is an alternative fuel that is a renewable energy with a lower cost rather than petrol itself. Biopetrol from palm oil is biodegradable and non-toxic. From the environmental point view, all the fuel from vegetable sources is environmentally friendly.

From the technical point of view, biofuel (biopetrol) is technically compatible with current internal combustion engine. Slight modification might be required to enhance the power. Biopetrol can be the solution for the future air emission control.

The application of existing biodiesel from palm oil in motor vehicle (diesel engine) has been proven successful. However its commercial viability requires further in depth study (Mansur, 2005).

There are four primary reasons for encouraging the development of biopetrol in Malaysia:

- Provides market for excess production of palm oil.
- The prices of petroleum are increasing.
- Decreases the total import of petroleum.
- Fuel (biopetrol) from vegetable oil is renewable and environmental friendly.

2.4.2.2 Biopetrol from Palmitic Acid

Palmitic acid or hexadecanoic acid (CH_3 $(CH_2)_{14}COOH$) is a fatty acid which is found in animal fats and vegetable oils.

To produce isooctane from palmitic acid, thermal cracking process is needed. Heat is supplied at palmitic acid's melting point within a range of 63^0C – 64^0C to melt the solid palmitic acid. After it turns to the liquid, the heating must be continuous until the isooctane's boiling point of 98^0C by using heating mantel to form new arrangements of carbon compounds including isooctane.

The sample produced will have lots of hydrocarbon chains because of the heat that breaks the carbon chain randomly. Although alkanes from C_5 until C_9 are categorized as gasoline, C_8 will be the major component in this study.

2.5 Overview on petroleum refining process

Petroleum is a complex mixture of organic compounds, most of which are alkanes and aromatic hydrocarbons. It also contains small amounts of oxygen (O), nitrogen (N), and sulfur (S). Mixtures of alkanes are perfectly suitable for uses in fuels, solvents and lubricants.

As we learned from history, alchemists of the middle Ages attempted to change base metals into gold by practicing wizardry. In a sense, refiners could be regarded as the modern day heirs apparent to these medieval sorcerers by transforming crude oil into a variety of useful and valuable products. Instead of using magic, however, refiners employ chemical science and processing technology to perform their unique brand of metamorphosis. Spread out over a number of acres, a refinery is a remarkable maze of metal, machinery and manpower. Towers, tanks, process vessels, pipelines, pumps, heat exchangers and compressors are just some of the components of a modern refinery. Operators, engineers, researchers, technicians, craftsmen and maintenance personnel are among those needed to keep a refinery running round-the-clock. A refinery consists of a number of different units, each with a specific purpose, integrated into a processing sequence.

The petroleum industry refines crude oil to obtain useful products. Refineries and chemical plants account for about a fifth of the industry's total investment in property and equipment. The United States has about 300 refineries that range in capacity from 40 to 365,000 barrels of oil a day. The world's largest refinery is in Abadan, Iran. It can process 412,000 barrels daily when running at full capacity. Hydrocarbons contain a lot of energy. Many of the things derived from crude oil like gasoline, diesel fuel, paraffin wax and so on take advantage of this energy.

Hydrocarbons can take on many different forms. The smallest hydrocarbon is methane (CH_4), which is a gas that is lighter than air. Longer chains with 5 or more carbons are liquids. Very long chains are solids like wax or tar. By chemically cross-linking hydrocarbon chains can be everything from synthetic rubber to nylon to the plastic in Tupperware. The major classes of hydrocarbons in crude oils include Paraffin, Aromatics, Napthenes or Cycloalkanes, and other hydrocarbons.

Distillation, or fractioning, is the first step in the refining process. It separates the various fractions of crude oil. The fact that different hydrocarbons vaporize (boil) at different temperatures makes possible the process of distillation. Table 2.3 below shows the boiling pint differences for hydrocarbon cracking.

Table 2.3 : Boiling point differences for hydrocarbon cracking (Solomons, 1997)

Boiling Range of Fraction	Number of Carbon Atoms per Molecule	Use
Below 20	C1 – C4	Natural Gas, bottled gas, petrochemicals
20 – 60	C5 – C6	Petroleum ether, solvents
60 – 100	C6 – C7	Ligroin, solvents
40 – 200	C5 – C10	Gasoline (straight run gasoline)
175 – 325	C12 – C18	Kerosene and jet fuel
250 – 400	C12 and higher	Gas oil, fuel oil, and diesel oil

Distillation is the evaporation and subsequent collection of a liquid that is a component in a mixture. Fractional distillation is the evaporation of two or more liquids from a parent mixture by using the differences in their boiling points. Both processes may be used for purification or separation.

A typical example of fraction distillation is in the separation of various hydrocarbons, for instance, butane, pentane from a hydrocarbon mixture that result from some process in the overall refining process. In this example, a refinery fractional distillation apparatus is commonly termed a fractional distillation column or a fractionating column and can be several hundred feed high, depending on the refinery throughput (Soares, 2001).

In the petroleum refining, this distillation process is started by running crude oil into pipes that pass through a furnace. As the oil is heated, the fractionated gasoline vaporizes first, followed by kerosene. At higher temperatures, such oil fractions as diesel oil and lubricant stocks boil. The mixture of hot vapors and liquid goes into a fractionating tower, which consisting bubble-cap trays. The vapor rises through the tower, which separates the fractions in a continuous process.

This separation of petroleum into its various fractions takes place in a crude distillation tower. Crude oil is first heated in a furnace. The resulting mixture of hot vapors and liquid is pumped into the closed, vertical distillation tower, which is sometimes as high as 100 feet. As the vapors rising, they are cooled and condensed at various levels and temperatures where they are trapped by a number of horizontal bubble-cap trays. The trays on the upper levels collect the lighter petroleum fractions such as naphtha (straight-run gasoline) and kerosene. Middle trays collect components such as light heating oil and diesel fuel. Heavy fuel oils asphalt and pitch fractions settle on lower trays. For example, heavy fuel oils condense at the bottom of the tower, and gasoline condenses at the top.

2.6 Conversion oil refining

2.6.1 Cracking

Cracking is a petroleum refining process in which heavy-molecular weight hydrocarbons are broken up into light hydrocarbon molecules by the application of heat and pressure, with or without the use of catalysts, to derive a variety of fuel products. Cracking is one of the principal ways in which crude oil is converted into useful fuels such as motor gasoline, jet fuel, and home heating oil. There are two type of cracking process which are thermal cracking and catalytic cracking.

The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are re-vaporized before cracking.

There is not any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:

$$C_{15}H_{32} \longrightarrow \underset{\text{ethene}}{2C_2H_4} + \underset{\text{propene}}{C_3H_6} + \underset{\text{octane}}{C_8H_{18}}$$

Or, showing more clearly what happens to the various atoms and bonds as shown in Figure 2.1:

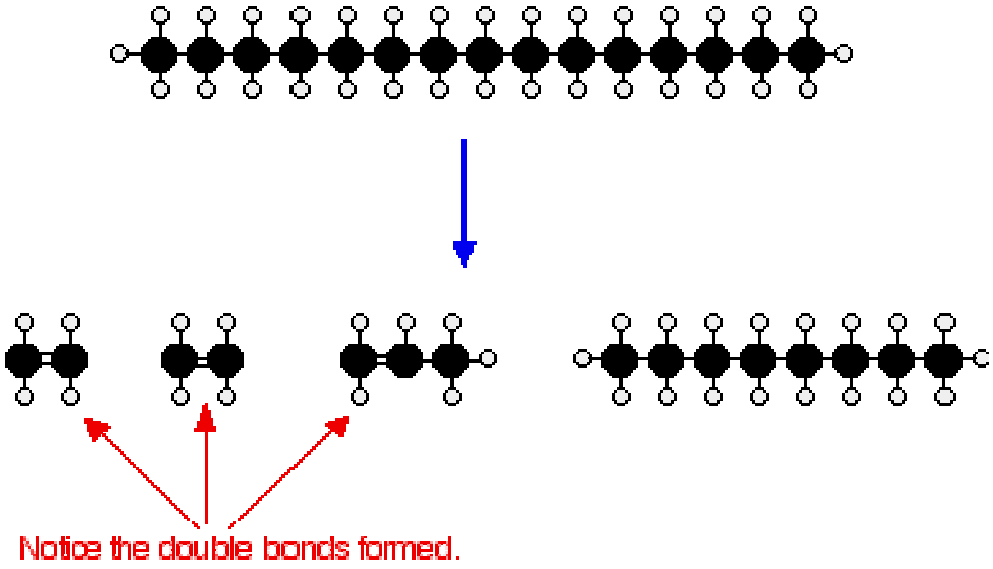

Figure 2.1 : Hydrocarbon Break Up Structure (Clark, 2003).

This is only one way in which this particular molecule might break up. The ethene and propene are important materials for making plastics or producing other organic chemicals. The octane is one of the molecules found in petrol (gasoline).

2.6.1.1 Thermal cracking

Thermal cracking is a refining process in which heat (~800 °C) and pressure (~700 kPa) are used to break down, rearrange, or combine hydrocarbon molecules. The first thermal cracking process was developed around 1913. Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics. However, this method produced large amounts of solid, unwanted coke.

The main reactions of thermal cracking include:

1. Initiation reactions, where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.

   $CH_3CH_3 \rightarrow 2\ CH_3\bullet$

2. Hydrogen abstraction, where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.

   $CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet$

3. Radical decomposition, where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.

   CH3CH2• → CH2=CH2 + H•

4. Radical addition, the reverse of radical decomposition, in which a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.

   $CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet$

5. Termination reactions, which happen when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are recombination, where the two radicals combine to form one

larger molecule, and disproportionation, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.

$$CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3$$

$$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3$$

Thermal cracking is an example of a reaction in which energies are dominated by entropy ($\Delta S°$) rather than by enthalpy ($\Delta H°$) in the free equation $\Delta G° = \Delta H° - T\Delta S°$. Although the bond dissociation energy D for a carbon-carbon single bond is relatively high (about 375 kJ/mol) and cracking is highly endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the extremely high temperature, makes $T\Delta S°$ term larger than the $\Delta H°$ term, thereby favoring the cracking reaction.

Thermal cracking doesn't go via ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed as shown in Figure 2.2.

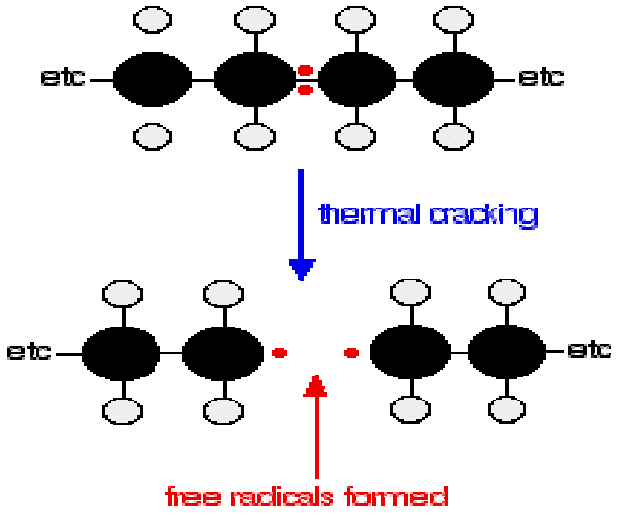

Figure 2.2 : Thermal Cracking Break Up Structure (Clark, 2003)

Reactions of the free radicals lead to the various products.

2.6.1.2 Catalytic cracking

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, liquified petroleum gas (LPG), heating oil, and petrochemical feedstock.

Catalytic cracking is similar to thermal cracking except that the additional catalysts facilitate the conversion of the heavier molecules into smaller molecules of desirable products. Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking.

Typical temperatures are from 450°-510°C at much lower pressures of 10-20 psi to aid the process of breaking down large hydrocarbon molecules into smaller ones. During this process, less reactive, and therefore more stable and longer lived intermediate cations accumulate on the catalysts' active sites generating deposits of carbonaceous products generally known as coke. Such deposits need to be removed (usually by controlled burning) in order to restore catalyst activity.

The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudites.

The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms - particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.